

SILICA, CRYSTALLINE by IR

7602

SiO ₂	MW: 60.08	CAS: 14808-60-7 (quartz) 14464-46-1 (cristobalite) 15468-32-3 (tridymite)	RTECS: VV7330000 (quartz) VV7325000 (cristobalite) VV3350000 (tridymite)
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METHOD: 7602, Issue 2

EVALUATION:

Issue 1: 15 February 1984

Issue 2: 15 August 1994

OSHA : quartz (respirable): 10 mg/m³/(% SiO₂ + 2);
cristobalite and tridymite (respirable): 1/2 the above

NIOSH: 0.05 mg/m³; carcinogens

ACGIH: quartz (respirable) 0.1 mg/m³
cristobalite (respirable) 0.05 mg/m³
tridymite (respirable) 0.05 mg/m³

PROPERTIES: solid; crystalline transformations:
quartz to tridymite @ 867 °C; tridymite to
cristobalite @ 1470 °C; α -quartz to
 β -quartz @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide

SAMPLING		MEASUREMENT	
SAMPLER:	CYCLONE + FILTER (10-mm nylon, or Higgins-Dewell (HD) + 0.8-µm or 5-µm PVC or MCE membrane)	TECHNIQUE:	INFRARED ABSORPTION SPECTROPHOTOMETRY
FLOW RATE:	nylon cyclone: 1.7 L/min HD cyclone: 2.2 l/min	ANALYTE:	quartz
VOL-MIN:	400 L	ASH:	muffle furnace or RF plasma asher
-MAX:	800 L	PELLET:	mix residue with KBr; press 13 mm pellet
SHIPMENT:	routine	IR:	scan absorbance from 1000 to 600 cm ⁻¹
SAMPLE STABILITY:	stable	CALIBRATION:	quartz diluted in KBr
BLANKS:	2 to 10 field blanks per set	RANGE:	10 to 160 µg quartz
BULK SAMPLE:	required; area respirable or settled dust	ESTIMATED LOD:	5 µg quartz
		PRECISION (\hat{S}_r):	< 0.15 @ 30 µg quartz per sample, in coal dust [1]
ACCURACY			
RANGE STUDIED:	not studied		
BIAS:	unknown		
OVERALL PRECISION (\hat{S}_{rT}):	not determined		
ACCURACY:	not determined		

APPLICABILITY: The working range is 0.025 to 0.4 mg/m³ for a 400-L air sample. Cristobalite and tridymite also have major absorbance peaks at 800 cm⁻² which can be used for their determination [1-6].

INTERFERENCES: Amorphous silica, calcite, cristobalite, kaolinite and tridymite interfere; see APPENDIX.

OTHER METHODS: This is P&CAM 110 [1]. It is similar to Method 7603, except for sample preparation (KBr pellet vs. redeposition). Crystalline silica can also be determined by X-ray diffraction (Method 7500) and spectrophotometry (Method 7601). XRD can distinguish the three polymorphs and does not detect amorphous silica. Silicates, which interfere with XRD, are removed by phosphoric acid cleanup.

REAGENTS:

1. Quartz* (NIST SRMs # 1878 and 2679, Standard Reference Materials Program, Rm 204, Bldg. 202, National Institute of Standards and Technology, Gaithersburg, MD 20899).
2. Potassium bromide (KBr), infrared quality.
3. Ethanol, 95% for cleaning sample handling equipment.*
4. Hydrochloric acid, 9% w/w. Dilute 25 mL conc. HCl (37% w/w) to 100 mL with deionized water.
5. Calibration stock standard, 0.5% w/w. Accurately weigh and thoroughly mix 5 g KBr (dried overnight at 110 °C) with 25 mg quartz. Store in a bottle in a desiccator.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
 - a. Filter: 37-mm diameter, 5.0- μ m pore size, polyvinyl chloride filter supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
 - b. Cyclone: 10-mm nylon or Higgins-Dewell (HD), or equivalent.
 - c. Sampling head holder: Holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
2. Area air sampler: PVC membrane filter, 37-mm, 5- μ m pore size in two piece filter cassette. Sample closed-face at 3 L/min.
3. Sampling pumps for HD cyclone, 2.2 L/min; nylon cyclone, 1.7 L/min; and area sampler, 3 L/min.
4. Infrared spectrophotometer; laboratory press for preparing KBr pellets; 13-mm KBr pellet die (evacuatable).
5. Low-temperature (RF Plasma) asher and aluminum weighing pans or muffle furnace and porcelain crucibles.
6. Mortar and pestle, 50 mm agate or mullite metal microspatula; non-serrate, non-magnetic forceps; desiccator, camel's hair brush, glassine paper.
7. Analytical balance (0.01 mg) for preparing standards.
8. Membrane filtration apparatus, 37-mm.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [1].

Ethanol is flammable. Keep away from flames.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at $1.7 \pm 5\%$ L/min with nylon cyclone or $2.2 \pm 5\%$ with HD cyclone for a total sample size of 400 to 800 L. Do not exceed 2 mg total dust loading on the filter.
NOTE: Do not allow the sampler assembly to be inverted at any time when using a cyclone. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.

SAMPLE PREPARATION:

3. Use one of the following methods to ash samples and blanks:
 - a. **Low temperature (RF Plasma) asher** Place the filters in labelled aluminum dishes (previously rinsed with distilled water, followed by ethanol, and air dried). Place the dishes

in the low temperature asher so that sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. Carefully bring asher to atmospheric pressure and remove the dishes.

- b. **Muffle furnace:** For samples containing a significant amount of calcite (> 20% of the total dust loading), wash filters with 9% w/w hydrochloric acid. Other samples proceed to step 3.b.ii.
 - i. Place a 0.5- μ m, 47-mm PVC filter in the filtration apparatus. Remove sample filter from cassette and center on top of first filter. Clamp funnel over the frit so that dust deposit is completely exposed. Add 10 mL 9% w/w HCl and 5 mL 2-propanol; allow to stand 5 min. Apply vacuum and slowly aspirate the acid and alcohol in the funnel. Wash with three successive 10-mL portions of distilled water. Release vacuum.
 - ii. Place filter samples and blanks in porcelain crucibles, loosely cover, and ash in muffle furnace for 2 h at 600 °C (800 °C if graphite is present).
4. Add approximately 300 mg KBr, weighed to 0.1 mg and dried overnight at 110 °C, directly to each sample. Mix the sample ash and KBr thoroughly with a pestle. Transfer to mortar to complete mixing if necessary. Transfer the mixture to a 13-mm evacuable pellet die using glassine paper and camel's hair brush. Press a pellet using standard technique. Weight the finished pellet to 0.1 mg. Calculate the ratio (weight of finished pellet/weight KBr initially added); it is usually about 0.98. Clean sample handling equipment with ethanol between samples.
NOTE: A low relative humidity environment will facilitate sample handling when using KBr.

CALIBRATION AND QUALITY CONTROL:

5. Prepare working standard pellets:
 - a. Weigh, to 0.001 mg, portions of calibration stock standard containing 10 to 200 μ g quartz.
 - b. Add an accurately-weighed 300 mg KBr. Proceed as in step 4.
 - c. Calculate the ratio (weight of finished pellet/weight of solids added); usually about 0.98.
 - d. Determine the absorbance at 800 cm^{-1} for each standard pellet following the analytical procedure (step 8). Plot absorbances vs. $\mu\text{g SiO}_2$.
6. If samples were low temperature ashed (step 3.a.) and kaolinite is present, prepare pellets containing 100 to 600 μ g kaolinite. Determine the absorbance at 800 cm^{-1} and at 915 cm^{-1} as abscissa. Prepare at least five different kaolinite concentrations. Use this curve to correct the absorbance value at 800 cm^{-1} for any sample containing kaolinite.
7. Carry media blanks and filters spiked with known amounts of quartz through the sample preparation procedures (steps 3 and 4) to monitor for contamination and losses.

MEASUREMENT:

8. Set the infrared spectrophotometer to absorbance mode and to the appropriate settings for quantitative analysis. Scan the pellet from 1000 cm^{-1} to 600 cm^{-1} . Rotate the pellet 45° and scan this diameter. Repeat twice more until 4 scans have been obtained. If the peak at 800 cm^{-1} is small, use 5X ordinate expansion to enhance the peak height. Draw an appropriate baseline under the absorbance band at 800 cm^{-1} from approximately 820 to 670 cm^{-1} . Measure the absorbance at 800 cm^{-1} from maximum to baseline in absorbance units. Average the four values for each sample.
9. If the sample was ashed at low temperature (step 3.a), the presence of kaolinite will be indicated by an absorption band with a maximum at 915 cm^{-1} . Draw an appropriate baseline under this band from approximately 960 to 860 cm^{-1} and measure the absorbance at 915 cm^{-1} from this baseline to the maximum.

CALCULATIONS:

10. Correction for kaolinite. Determine the sample absorbance at 915 cm^{-1} (step 9), refer to the kaolinite curve (step 6) to find the absorbance at 800 cm^{-1} . Use this corrected value in step 11.
11. If correction for kaolinite is not required, use the absorbance at 800 cm^{-1} to find the weight of quartz, W_q (μg), from the calibration graph.
12. Calculate the concentration of silica, C (mg/m^3), in the volume of air sampled, V (L):

$$C = \frac{W_q}{V}, \text{ mg}/\text{m}^3.$$

13. If percent quartz, % Q, is required, divide the weight of quartz, W_q (μg), by the total sample weight, W_s (μg):

$$\% Q = \frac{W_q}{W_s} \cdot 100.$$

EVALUATION OF METHOD:

This method is based on the well-characterized infrared method [1]. This method is particle size dependent. A mismatch of standards and sample particle sizes will result in an uncorrectable bias. A thorough study of the range of biases in IR methods has not been done.

REFERENCES:

- [1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 110, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
- [2] Talvitie, N.A. Determination of Quartz in the Presence of Silicates Using Phosphoric Acid, Anal. Chem., **23**, 623-626 (1951).
- [3] Larsen, D.J., L.J. von Loenhoff and J.V. Crable. The Quantitative Determination of Quartz in Coal Dust by Infrared Spectroscopy, Am. Ind. Hyg. Assoc. J., **33**; 367-372 (1972).
- [4] Dodgson, J. and W. Whittaker. The Determination of Quartz in Respirable Dust Samples by Infrared Spectrophotometry-1: The Potassium Bromide Disc Method, Ann. Occup. Hyg., **16**; 373-387 (1973).
- [5] Cares, J.W., A.S. Goldin, J.J. Lynch and W.A. Burgess. The Determination of Quartz in Airborne Respirable Granite Dust by Infrared Spectrophotometry, Am. Ind. Hyg. Assoc. J., **34**; 298-305 (1973).
- [6] Taylor, D.G., C.M. Nenadic and J.V. Crable. Infrared Spectra for Mineral Identification, Am. Ind. Hyg. Assoc. J., **31**, 100-108 (1970).
- [7] Criteria for a Recommended Standard...Occupational Exposure to Crystalline Silica, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-120 (1974).

METHOD REVISED BY:

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APPENDIX:**INTERFERENCES**

Quartz and cristobalite can be determined in each other's presence by the use of less sensitive bands at 695 cm^{-1} (quartz) and 625 cm^{-1} (cristobalite). Tridymite can only be determined in the absence of the other two polymorphs; it is rarely encountered in industrial hygiene samples. Interfering silicates can be removed using a phosphoric acid cleanup procedure [2].

Cristobalite and tridymite interfere positively at the 800 cm^{-1} peak, although they are rarely present in industrial hygiene samples. Kaolinite, a common component of coal, can interfere when RF plasma ashing is used to remove the collection filter, if it is present in sufficient quantity. A correction procedure is outlined in the method (steps 6 and 10). Calcite, at greater than 20% of the total dust loadings, can interfere by reacting with the quartz during muffle ashing. A procedure for its removal is given (step 3.b). Amorphous silica may interfere if present in large amounts. This interference can be minimized by accounting for its broad absorbance band when drawing the baseline.